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(54) Title: CEMENT SUPERPLASTICISER

(57) Abstract: The invention provides a superplasticiser for cement and concrete obtained by condensing with formaldehyde a sulfonated aromatic compound; and a naphthalene derivative, substituted at any position with R<sub>1</sub>, R<sub>2</sub> and R<sub>3</sub>, wherein R<sub>1</sub>, R<sub>2</sub> and R<sub>3</sub> are independently selected from H, (CH<sub>2</sub>)<sub>n</sub>OH (n=0 to 6), N(CH<sub>2</sub>CH<sub>2</sub>OH)<sub>2</sub>, O(CH<sub>2</sub>CH<sub>2</sub>O)<sub>n</sub>H (n=1 to 113), CH<sub>2</sub>O(CH<sub>2</sub>CH<sub>2</sub>O)<sub>n</sub>CH<sub>3</sub> (n=1 to 113), O(CH<sub>2</sub>CH<sub>2</sub>O)<sub>n</sub>CH<sub>3</sub> (n=1 to 113), (CH<sub>2</sub>)<sub>n</sub>COOH (n=0 to 6), and O(CH<sub>2</sub>)<sub>n</sub>COOH (n=1 to 6), and R<sub>3</sub> is selected from H and CH<sub>2</sub>OH; and/or a benzene derivative, substituted at any position with R<sub>4</sub>, R<sub>5</sub> and R<sub>6</sub>, wherein R<sub>4</sub>, R<sub>5</sub> and R<sub>6</sub> are independently selected from H, (CH<sub>2</sub>)<sub>n</sub>OH (n=0 to 6), N(CH<sub>2</sub>CH<sub>2</sub>OH)<sub>2</sub>, O(CH<sub>2</sub>CH<sub>2</sub>O)<sub>n</sub>H (n=1 to 113), CH<sub>2</sub>O(CH<sub>2</sub>CH<sub>2</sub>O)<sub>n</sub>CH<sub>3</sub> (n=1 to 113), O(CH<sub>2</sub>CH<sub>2</sub>O)<sub>n</sub>CH<sub>3</sub> (n=1 to 113), (CH<sub>2</sub>)<sub>n</sub>COOH (n=1 to 6), and O(CH<sub>2</sub>)<sub>n</sub>COOH (n=1 to 6), and R<sub>6</sub> is selected from H and NH<sub>2</sub>; wherein the superplasticiser comprises at least one monomer that has at least one carboxyl group, and at least one monomer that has at least one hydroxyl group.



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## CEMENT SUPERPLASTICISER

### TECHNICAL FIELD OF THE INVENTION

The invention relates to the field of cement additives, specifically  
5 superplasticisers.

### BACKGROUND ART

Superplasticisers are chemical admixtures, which can maintain an  
adequate workability of fresh concrete at low water/cement ratios, for a  
10 reasonable period of time, preferably without affecting the setting and  
hardening behaviour of the cementitious system. Concrete prepared at  
low water/cement ratios will exhibit lower porosity and will thus show  
enhanced strength and durability.

In order to be classified as a superplasticiser (high range water  
15 reducer) the chemical admixture must be able to reduce by 15 to 30% the  
water required to produce a workable concrete.

In chemical terms, superplasticisers are organic polyelectrolytes,  
which belong to the category of polymeric dispersants, and are  
considered as "specialised" dispersing admixtures. Actually, the most  
20 commonly used superplasticiser polymers are sulfonated aromatics  
condensed with formaldehyde. Two such products were developed and  
optimised: one uses naphthalene as the aromatic building block yielding  
polynaphthalene sulfonate (PNS); the other uses melamine which leads to  
polymelamine sulfonate (PMS). These two types of products can achieve  
25 comparable water reduction when used at their respective optimal  
dosage, although they exhibit minor differences in some practical aspects  
of their application. The main limitation currently reported for these  
products is their inability to retain the initial slump of the fresh concrete  
for an extended period, ideally two hours.

Much work has been done to develop new superplasticisers that increase the slump time of fresh concrete without detracting from the qualities of the hardened concrete product. In U.S. patent no. 5,880,182 (incorporated herein by reference), polycarboxylates are used in conjunction with saccharides. Polycarboxylates can act as very effective superplasticisers. However, polycarboxylate superplasticisers are expensive to produce, making their use less competitive.

Superplasticisers based on naphthalene sulfonate are particularly attractive because of their cost effectiveness. Attempts have been made to increase the slump retention qualities of naphthalene sulfonate/formaldehyde condensates. For example, U.S. patent no. 5,651,817 (incorporated herein by reference) discloses two kinds of superplasticisers: 1) superplasticisers consisting of a copolymer produced by condensation of an oxyethylene- or oxypropylene-aryl compound and an aromatic carboxylic acid with formaldehyde, and 2) superplasticisers consisting of a copolymer produced by condensation of an oxyethylene- or oxypropylene-aryl compound, an aromatic carboxylic acid and an aromatic sulfonate with formaldehyde.

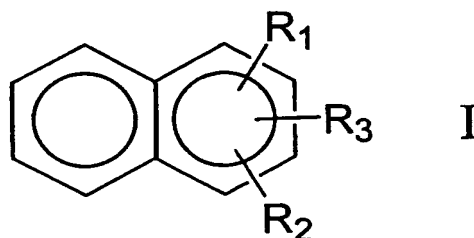
In the same vein, U.S. patent no. 4,759,802 (incorporated herein by reference) discloses the introduction of hydroxy and carboxylate groups into a naphthalene sulfonate/formaldehyde condensate by partial oxidation of the condensate.

Japanese patent no. 60033240 discloses superplasticisers consisting of a formaldehyde condensate with naphthalene sulfonate and naphthalene carboxylic acid.

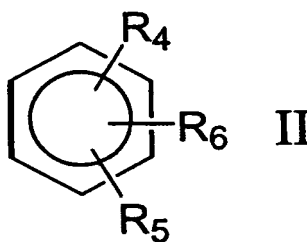
## DISCLOSURE OF THE INVENTION

## SUMMARY OF THE INVENTION

The present invention provides in a first aspect a polymer obtained  
 5 by condensing with formaldehyde the monomers (A) a sulfonated  
 aromatic compound; and (B):



wherein  $R_1$ ,  $R_2$  and  $R_3$  may be substituted at any position of either  
 10 aromatic ring, and are independently selected from H,  $(CH_2)_nOH$  ( $n=0$  to  
 6),  $N(CH_2CH_2OH)_2$ ,  $O(CH_2CH_2O)_nH$  ( $n=1$  to 113),  $CH_2O(CH_2CH_2O)_nCH_3$   
 ( $n=1$  to 113),  $O(CH_2CH_2O)_nCH_3$  ( $n=1$  to 113),  $(CH_2)_nCOOH$  ( $n=0$  to 6), and  
 $O(CH_2)_nCOOH$  ( $n=1$  to 6), and  $R_3$  is selected from H and  $CH_2OH$ ; and/or  
 (C):

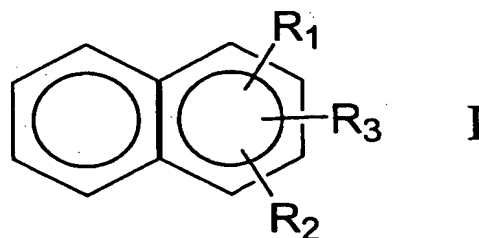


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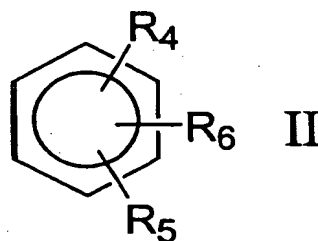
wherein  $R_4$ ,  $R_5$  and  $R_6$  may be substituted at any position of the  
 benzene ring, and are independently selected from H,  $(CH_2)_nOH$  ( $n=0$  to  
 6),  $N(CH_2CH_2OH)_2$ ,  $O(CH_2CH_2O)_nH$  ( $n=1$  to 113),  $CH_2O(CH_2CH_2O)_nCH_3$   
 ( $n=1$  to 113),  $O(CH_2CH_2O)_nCH_3$  ( $n=1$  to 113),  $(CH_2)_nCOOH$  ( $n=1$  to 6), and  
 20  $O(CH_2)_nCOOH$  ( $n=1$  to 6), and  $R_6$  is selected from H and  $NH_2$ ;

wherein the polymer comprises at least one monomer that has at least one carboxyl group, and at least one monomer that has at least one hydroxyl group.

In a second aspect, the invention provides a superplasticiser for fresh concrete, the superplasticiser being obtained by condensing with formaldehyde the monomers (A) a sulfonated aromatic compound; and (B):



wherein  $R_1$ ,  $R_2$  and  $R_3$  may be substituted at any position of either aromatic ring, and are independently selected from H,  $(CH_2)_nOH$  ( $n=0$  to 6),  $N(CH_2CH_2OH)_2$ ,  $O(CH_2CH_2O)_nH$  ( $n=1$  to 113),  $CH_2O(CH_2CH_2O)_nCH_3$  ( $n=1$  to 113),  $O(CH_2CH_2O)_nCH_3$  ( $n=1$  to 113),  $(CH_2)_nCOOH$  ( $n=0$  to 6), and  $O(CH_2)_nCOOH$  ( $n=1$  to 6), and  $R_3$  is selected from H and  $CH_2OH$ ; and/or (C):



15

wherein  $R_4$ ,  $R_5$  and  $R_6$  may be substituted at any position of the benzene ring, and are independently selected from H,  $(CH_2)_nOH$  ( $n=0$  to 6),  $N(CH_2CH_2OH)_2$ ,  $O(CH_2CH_2O)_nH$  ( $n=1$  to 113),  $CH_2O(CH_2CH_2O)_nCH_3$  ( $n=1$  to 113),  $O(CH_2CH_2O)_nCH_3$  ( $n=1$  to 113),  $(CH_2)_nCOOH$  ( $n=1$  to 6), and  $O(CH_2)_nCOOH$  ( $n=1$  to 6), and  $R_6$  is selected from H and  $NH_2$ ;

20

wherein the superplasticiser comprises at least one monomer that has at least one carboxyl group, and at least one monomer that has at least one hydroxyl group.

In a third aspect, the invention provides a method for decreasing  
5 the water requirement of a fresh concrete composition comprising adding to cement a plasticising amount of a superplasticiser according to the invention.

In a fourth aspect, the invention provides a dry cement composition, comprising cement and a superplasticiser according to the  
10 invention.

In a fifth aspect, the invention provides a wet fresh concrete composition comprising a dry cement composition, according to the invention, mixed with water.

In a sixth aspect, the invention provides a cured concrete product  
15 produced by curing a wet fresh concrete composition according to the invention.

## DETAILED DESCRIPTION OF THE INVENTION

### 20 BRIEF DESCRIPTION OF THE DRAWINGS

Preferred embodiments of the invention will be described with the aid of the drawings, which show:

Figure 1 shows the slumps of fresh concrete (Lafarge T-10 cement) at 10, 30, 45, 60 and 120 minutes, using different wt %'s of a  
25 superplasticiser having a molar composition of 91 molar % naphthalene sulfonate and 9 molar % 3-hydroxy-2-naphthoic acid (BON), in comparison with fresh concrete prepared with polynaphthalene sulfonate (regular pNS) as superplasticiser.

Figure 2 shows the slump loss obtained with St. Lawrence Cement and 0.5 wt% superplasticiser of the invention (Example 7), in comparison with 0.6 wt% pNS.

Figure 3 shows the slump loss obtained with Holnam Cement and 0.6 wt% superplasticiser of the invention (Example 7), in comparison with 0.6 wt% pNS.

Figure 4 shows the initial and final setting times (in hours and minutes) for Lafarge T-10 cement with 0.6 wt% superplasticiser of the invention (Example 7), in comparison with 0.7 wt% pNS.

Figure 5 shows compressive strength (in Mpa) at 1, 7 and 28 days for concrete prepared with 0.6 wt% superplasticiser of the invention (Example 7), in comparison with 0.7 wt% pNS.

Figure 6 shows the slump of fresh concrete (Lafarge T-10 cement) at 10, 30, 45, 60 and 90 minutes, using 0.6 wt % superplasticiser of the invention (Example 7), in comparison with fresh concrete prepared with 0.2 wt% of an acrylic ester copolymer ("polycarboxylate") as superplasticiser.

Figure 7 shows the air content at 10 and 90 minutes of fresh concrete prepared with 0.6 wt% superplasticiser of the invention (Example 7) in comparison with concrete prepared with 0.2 wt% polycarboxylate superplasticiser.

Figure 8 shows the initial and final setting times (in hours and minutes) for Lafarge T-10 cement with 0.6 wt% superplasticiser of the invention (Example 7), in comparison with 0.2 wt% polycarboxylate superplasticiser.

Figure 9 shows compressive strength (in Mpa) at 1, 7 and 28 days for concrete prepared with 0.6 wt% superplasticiser of the invention

(Example 7), in comparison with 0.2 wt% polycarboxylate superplasticiser.

The polymers of the invention are in themselves novel. They demonstrate superior plasticising ability in fresh concrete, extending slump  
5 time while not substantially increasing setting time, and without exhibiting any detrimental effect on the quality of the hardened concrete product.

Preferred compounds for the sulfonated aromatic monomer (A), are those having 6 to 10 carbon atoms in the aromatic nucleus. Preferred are those bearing one sulfonate group. The sulfonated aromatic monomer  
10 may also bear up to four ( $C_1$ - $C_6$ )alkyl groups as substituents on the aromatic nucleus. Examples of compounds suitable as monomer (A) are benzene sulfonate, naphthalene sulfonate, sulfosalicylic acid, sulfophthallic acid, xylene sulfonic acid, toluene sulfonic acid, sulfanilic acid, sulfobenzoic acid, ( $C_1$ - $C_6$ )alkylbenzene sulfonates and ( $C_1$ -  
15  $C_6$ )alkylnaphthalene sulfonates. Preferred is naphthalene sulfonate, particularly  $\beta$ -naphthalene sulfonate.

In polymers in which only monomer (A) and monomer (B) are used, it is preferred that in the monomer (B), one of  $R_1$  and  $R_2$  be a group containing an OH group, for example  $(CH_2)_nOH$  ( $n=0$  to 6), or  
20  $N(CH_2CH_2OH)_2$ , and the other be a group containing a carboxyl group, for example  $(CH_2)_nCOOH$  ( $n=0$  to 6), or  $O(CH_2)_nCOOH$  ( $n=1$  to 6). It is particularly preferred that one of  $R_1$  and  $R_2$  be OH, and the other be COOH. The substituents  $R_1$  and  $R_2$  may be at any position in either of the rings of the naphthalene nucleus. Some examples of compounds suitable  
25 as monomer (B) for preparing a polymer of the invention are 3-hydroxy-2-naphthoic acid (BON) (i.e.  $R_1$  is 3-OH,  $R_2$  is 2-COOH, and  $R_3$  is H) and 4-hydroxymethyl-3-hydroxy-2-naphthoic acid (i.e.  $R_1$  is 3-OH,  $R_2$  is 2-COOH, and  $R_3$  is  $CH_2OH$ ).



Some examples of suitable compounds for use as monomer (C) include benzoic acid, o- m- and p- hydroxy benzoic acids, benzyl alcohol, phenylacetic acid, and phenoxyacetic acid.

The polymers of the invention can be obtained by two general routes, which for the purposes of this discussion, are called "one step" and "two step" methods. The one step method is carried out by condensing a mixture of formaldehyde (or formalin) and monomer (A) with at least one of monomers (B) and (C). Included in this are polymers produced by condensation with formaldehyde of monomer (A) and monomer (B), monomer (A) and monomer (C), and monomer (A) with both monomers (B) and (C).

Although the invention is described in terms of condensates with formaldehyde, it would be understood by one skilled in the art that other C<sub>1-6</sub> aldehydes would also work.

For the two step method, a homopolymer of a sulfonated aromatic compound ("poly-monomer (A)") is reacted with monomer (B), and/or monomer (C).

The polymers of the invention comprise at least one monomer with at least one carboxyl group, and at least one monomer with at least one hydroxyl group. The polymer should comprise at least about 1 molar % and can comprise up to 70 molar % of total monomer units which bear a COOH group (In the condensing reaction, the formaldehyde forms a linking methylene group between monomers. In this description, the linking methylene groups are not considered as monomers, and "molar %" in reference to a monomer, with respect to the total, does not include the linking methylene groups). Particularly effective superplasticisers are those in which about 4 molar % to about 10 molar % of the total monomer units bear a carboxyl group.

The polymers of the invention comprise at least one monomer bearing a hydroxyl group. The polymer should comprise at least about 1 molar % and can comprise up to 70 molar % of total monomer units which bear a hydroxyl group. Excellent plasticising properties are conferred if about 4 molar % to about 10 molar % of the total monomer units bear a hydroxyl group.

A preferred polymer of the invention is produced by condensing formaldehyde with naphthalene sulfonate and BON. Good plasticising properties are obtained using a polymer in which the monomer units are about 80 to 98 molar % naphthalene sulfonate and about 20 to 2 molar % BON. Excellent superplasticiser properties are obtained with a polymer in which the monomer units are about 94 molar % naphthalene sulfonate and about 6 molar % BON.

The polymers of the invention can be produced by methods known in the art. In a preferred method, monomer (A) and/or monomer (B) and/or monomer (C) and formalin are heated in water in the presence of an acid catalyst. A preferred acid catalyst is a mineral acid, such as sulphuric acid. The condensation causes the monomers to be linked by linking methylene groups.

The superplasticisers of the invention may be mixed with water and then added to cement, however, the invention further relates to a dry cement composition, comprising a polymer of the invention. The dry cement composition comprises, in addition to a polymer of the invention, at least cement, such as Portland cement, or high alumina cement. It may additionally comprise sand and fine aggregate such as gravel, and other cement additives known to one skilled in the art (see for example: Franklin, A.J.; *Cement and Mortar Additives*; Noyes Data Corp., USA, 1976; Gutcho, M.H.; *Cement and Mortar Technology and Additives*; Noyes Data

Corp., USA; Ramachandran, V.S.; *Concrete Admixtures Handbook*; Noyes Publications, USA, 1984; Ramachandran, V.S.; *Concrete Admixtures Handbook*; 2<sup>nd</sup> Edition, Noyes Publications, USA, 1995, all incorporated herein by reference).

5        The invention further relates to a wet fresh concrete composition, comprising a paste or slurry made by adding a polymer of the invention either as a solid, suspension or solution in water to a conventional cement mixture.

10        When used as superplasticisers, the polymers of the invention are added to a dry cement composition in amounts of from about 0.1 to 1.0 wt %, preferably 0.3 to 0.8 wt %, most preferably 0.6 to 0.7 wt %, based on the dry weight of the total cement composition (excluding fine aggregate and sand).

15        A cement composition according to the invention can be used to prepare a wet fresh concrete composition, with a decreased water requirement. The prepared wet fresh concrete compositions exhibit enhanced slump, and extended slump times. Slump and slump time for simple cement pastes may be measured according to a "mini-slump test", as described in *Cement, Concrete and Aggregates*; Kantro, D.L.; vol. 2, 1980, 20 pp 96-102., and slump and slump time for concrete may be measured in accordance with ASTM designation C 143-90a.

25        Cement compositions prepared with superplasticisers of the invention set within a convenient time frame, allowing construction workers to remove moulds for use elsewhere without undue waiting. The time of setting for hydraulic cement may be measured according to ASTM designations C 191-92, and C 403/C 403M-95.

Wet fresh concrete compositions according to the invention yield hardened concrete products with high compressive strengths and

excellent durability. Compressive strength may be measured according to ASTM designation C 39-94.

Preferred embodiments of the invention will be further described with reference to the following examples, which are not intended to limit  
5 the invention in any way.

*Example 1, "one step method", 94 molar % naphthalene sulfonate, 6 molar % BON*

A condensate of naphthalene sulfonate, BON and formaldehyde  
10 was prepared according to the "one step" method, in the following manner:

Naphthalene (256 g, 2.00 moles) and 98 % sulphuric acid (214 g, 2.14 moles) were charged into a two litre pressurised reactor, and heated for three hours at 160°C to produce naphthalene sulfonate, which was not  
15 isolated. The mixture was cooled to 110°C, and water (295 g), BON (25 g, 0.13 mole) mixed with water (25 g), and 37% formaldehyde (190 g, 2.34 moles) were added (addition of water first cools the mixture so that formaldehyde may be added). The molar percentages of naphthalene sulfonate and BON in the reaction mixture (based on the total of  
20 naphthalene sulfonate and BON) were approximately 94 molar % naphthalene sulfonate and approximately 6 molar % BON. The temperature was increased to 128-130°C and stirred for six hours at approximately 36 p.s.i. The mixture was then allowed to cool to 80°C and calcium hydroxide (58 g 38% slurry, 0.30 mole) and 50% sodium  
25 hydroxide (162 g, 2.03 moles) were added. After filtration, the product had the following characteristics:

	Solids (wt%)	41.57
	pH	9.21
	Viscosity (cps)	78.20
	Free formaldehyde (wt%)	0.14
5	Sulphate (wt%)	1.39

***Example 2, "one step method", 97 molar % naphthalene sulfonate, 3 molar % BON***

A second condensate of naphthalene sulfonate, BON and  
10 formaldehyde was prepared according to the "one step" method, as in  
Example 1, except that the BON was decreased to 12 g (0.06 mole) and 185  
g (2.28 mole) of formaldehyde were used. The molar percentages of  
naphthalene sulfonate and BON in the reaction mixture (based on the  
total of naphthalene sulfonate and BON) were approximately 97 molar %  
15 naphthalene sulfonate and approximately 3 molar % BON. After  
filtration, the product had the following characteristics:

	Solids (wt%)	41.22
	pH	8.58
	Viscosity (cps)	126.00
20	Free formaldehyde (wt%)	0.17
	Sulphate (wt%)	1.17

***Example 3, "two step method", with poly(naphthalene sulfonate) and BON***

25 A condensate of naphthalene sulfonate and formaldehyde (1585 g,  
1.679 moles expressed as  $C_{10}H_8$ ) was charged into a two litre pressurised  
reactor without isolation, with BON (41 g, 0.213 moles). The mixture was  
heated at 108°C for 1.5 hours, after which time it was cooled to 80°C and  
neutralised with lime and caustic to approximately pH 8. After filtration,  
30 the product had the following characteristics:

	Solids (wt%)	40.93
	pH	7.89
	Viscosity (cps)	79.70
	Free formaldehyde (wt%)	0.01
5	Sulphate (wt%)	1.18

***Example 4, "two step method", with poly(naphthalene sulfonate) and BON methylol***

4-hydroxymethyl-3-hydroxy-2-naphthoic acid, or BON methylol, was synthesised for use as a monomer, as follows: BON (25 g, 0.13 mole) NaOH (50%, 11g, 0.14 mole) and 37% formaldehyde (11 g, 0.14 mole) were heated in water (50 g) to approximately 75-80°C at pH 9-10 for 1 hour. Without isolation, the BON methylol was charged into a two litre pressurised reactor with a naphthalene sulfonate/formaldehyde condensate (944 g, 1.00 mole, expressed as C<sub>10</sub>H<sub>8</sub>), and the resulting mixture was heated at 100°C for 1.5 hours. It was then cooled to 80°C and neutralised using lime and caustic to approximately pH 8. After filtration, the product had the following characteristics:

	Solids (wt%)	41.05
20	pH	8.22
	Viscosity (cps)	79.2
	Free formaldehyde (wt%)	0.17
	Sulphate (wt%)	1.49

***Example 5, "one step method", 83 molar % naphthalene sulfonate, 17 molar % naphthalene acetic acid***

Naphthalene was sulfonated as in example 1. The crude naphthalene sulfonate reaction mixture (765 g) was charged into a two litre pressurised reactor, and water (80 g), naphthalene acetic acid (75 g, 0.40 mole), 98 % sulphuric acid (6 g), and 37% formaldehyde (215 g, 2.65

moles), were added at approximately 80°C. The molar percentages of naphthalene sulfonate and naphthalene acetic acid in the reaction mixture (based on the total of naphthalene sulfonate and naphthalene acetic acid) were approximately 83 molar % naphthalene sulfonate and approximately 17 molar % naphthalene acetic acid. The temperature was increased to 128-130°C and held for 7 hours with stirring at approximately 36 p.s.i. The mixture was then cooled and neutralised with calcium hydroxide (71 g 38 % slurry, 0.36 mole) and 50 % sodium hydroxide (184 g, 2.30 moles). After filtration, the product had the following characteristics:

	Solids (wt%)	42.20
	pH	7.78
	Viscosity (cps)	41.2
	Free formaldehyde (wt%)	0.17
15	Sulphate (wt%)	0.86

***Example 6, "one step method", 88 molar % naphthalene sulfonate, 12 molar % BON methylol***

Naphthalene (256 g, 2.00 mol) was sulfonated with 98 % sulphuric acid (214 g, 2.14 moles) as in Example 1. After adding water (200 g), and cooling to approximately 80°C, to the reaction vessel were added a BON methylol reaction mixture synthesised according to Example 4 (219 g reaction mixture, containing 0.27 mole BON methylol), and 37 % formaldehyde (179 g, 2.21 moles). The temperature was increased to 128-130°C and held for 8 hours with stirring at approximately 37-40 p.s.i. After cooling to approximately 80°C, the mixture was neutralised with calcium hydroxide (58 g 38 % slurry, 0.30 mole) and 50% sodium hydroxide (135 g, 1.69 moles). After filtration, the product had the following characteristics:

	Solids (wt%)	41.34
	pH	8.36
	Viscosity (cps)	103
	Free formaldehyde (wt%)	0.17
5	Sulphate (wt%)	1.07

**Example 7, "one step method", 91 molar % naphthalene sulfonate, 9 molar % BON**

According to the method recited in Example 2, a superplasticiser  
 10 was made consisting of 91 molar % naphthalene sulfonate and 9 molar %  
 BON. The resulting polymer had the following characteristics:

	Example 7
Solids content (%w/w)	41.2
Insolubles (%v/v)	< 0.1
Sodium sulphate (%w/w)	1.8
pH of 41% solution	8.5
Specific gravity @25°C	1.20
Chlorides (ppm as Cl <sup>-</sup> )	60
Viscosity @ 25°C (cps)	75

In the above examples, it is possible to obviate the need for  
 15 filtering, by neutralising with a hydroxide or oxide (e.g. LiOH, KOH,  
 NaOH, MgO, Mg(OH)<sub>2</sub> or NH<sub>4</sub>OH alone or in combination) which will  
 not form an insoluble sulphate salt on reaction with the excess sulphuric  
 acid.



*Slump enhancing and prolonging characteristics of superplasticisers of the invention*

The above superplasticisers were tested for slump enhancing and prolonging characteristics in simple cement pastes, according to a "mini-slump test", as described in *Cement, Concrete and Aggregates*; Kantro, D.L.; vol. 2, 1980, pp 96-102. As a reference compound, the known superplasticiser polynaphthalene sulfonate (pNS) was used. For the slump trials, a weighed amount of cement was mixed with a solution of the superplasticiser in water, to produce cement paste. The superplasticisers were mixed with cement at various wt% concentrations, based on dry cement. The pastes were all prepared at a water/cement ratio of 0.35. Slump is measured using a standard inverted cone, open at the bottom. The cone is placed with its open bottom on a glass plate, and the cement paste is placed inside the cone. When the cone is lifted, if the cement paste is sufficiently fluid, it will flow out the bottom of the cone, forming a roughly circular blob of cement paste on the glass, which is commonly called a "pie". Slump can be reported as either the diameter or the area of the pie. The slumps for the pastes prepared using pNS and the superplasticisers of the invention were measured at intervals of 10, 30, 60, 90 and 120. The results are listed in Tables 1 to 4.

*Table 1. Slump (mm) versus time (minutes) for cement pastes prepared with pNS, Example 1 and Example 2 as superplasticisers (St. Laurent T-10 cement, water/cement ratio of 0.35)*

Superplasticiser used	pNS (reference)	Example 1	Example 2
Superplasticiser concentration (wt%) on dry cement basis	0.6	0.6	0.6
Time (min.)	Slump (mm)	Slump (mm)	Slump (mm)
10	178	202	194
30	174	196	185
60	143	180	170
90	126	171	151
120	107	163	140

- 5 From the results in Table 1, it is clear that the two plasticisers of the invention exhibit enhanced initial slump, when compared to the known superplasticiser, pNS, and also extend the slump time considerably. With the superplasticiser of Example 1, the slump after 120 minutes is comparable to the *initial* slump of a batch prepared with pNS.

**Table 2. Slump (mm) versus time (minutes) for cement pastes prepared with pNS, Example 3 and Example 4 as superplasticisers (St. Laurent T-10 cement, water/cement ratio of 0.35)**

Superplasticiser used	pNS (reference)	Example 3	Example 4
Superplasticiser concentration (wt%) on dry cement basis	0.6	0.6	0.6
Time (min.)	Slump (mm)	Slump (mm)	Slump (mm)
10	167	184	195
30	162	194	190
60	135	182	185
90	117	177	175
120	98	169	164

- 5 From the results in Table 2, it is clear that the two plasticisers of the invention exhibit enhanced initial slump, when compared to the known superplasticiser, pNS, and also extend the slump time considerably. With the superplasticiser of both Examples 3 and 4, the slump after 120 minutes is comparable to the *initial* slump of a batch prepared with pNS.

*Table 3. Slump (mm) versus time (minutes) for cement pastes prepared with pNS, and Example 5 as superplasticisers (Lafarge T-10 cement, water/cement ratio of 0.35)*

Superplasticiser used	pNS (reference)	Example 5
Superplasticiser concentration (wt%) on dry cement basis	0.7	0.7
Time (min.)	Slump (mm)	Slump (mm)
10	129	129
30	119	131
60	107	128
90	94	122
120	82	119

- 5 From the results in Table 3, it can be seen that the superplasticiser of Example 5 confers the same initial slump on the cement paste as pNS. However, unlike pNS, the superplasticiser of Example 5 maintains the slump at close to its initial level at 120 minutes.

**Table 4. Slump (mm) versus time (minutes) for cement pastes prepared with pNS, Example 1 and Example 6 as superplasticisers (Lafarge T-10 cement, water/cement ratio of 0.35)**

Superplasticiser used	pNS (reference)	Example 1	Example 6
Superplasticiser concentration (wt%) on dry cement basis	0.7	0.7	0.7
Time (min.)	Slump (mm)	Slump (mm)	Slump (mm)
10	163	169	175
30	159	167	173
60	154	165	171
90	145	157	166
120	141	153	160

5

**Comparison of a superplasticiser of the invention with pNS in fresh and hardened concrete**

**Tests on fresh concrete**

10        The performance of a superplasticiser of the invention (Example 7) was compared with that of polynaphthalene sulfonate ("regular pNS"). The properties of fresh and hardened concrete were investigated under different cements at a water to cement ratio of 0.30.

15        The composition of the different cements tested is indicated in Table 5. The fine aggregate was natural siliceous sand and the coarse aggregate was local metamorphic limestone having a maximum size of 20 mm.

**Table 5: Cement Composition**

	A (Lafarge Cement)	B (St-Lawrence Cement)	C (Holnam Cement)
SiO <sub>2</sub> (%)	20.6	22.3	20.9
Al <sub>2</sub> O <sub>3</sub>	4.4	4.0	5.1
Fe <sub>2</sub> O <sub>3</sub>	3.0	3.0	3.8
CaO	62.8	62.4	64.2
MgO	2.8	2.0	1.3
Na <sub>2</sub> O eq.	0.77	0.75	0.32
SO <sub>3</sub>	3.2	3.0	2.7
Loss on ignition	2.1	1.8	0.6

C <sub>3</sub> S	56	53	55
C <sub>2</sub> S	17	24	18
C <sub>3</sub> A	7	6	7
C <sub>4</sub> AF	9	9	12

Blaine Surface Area (m <sup>2</sup> /kg)	380	360	400
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Concrete (70ℓ or 170kg each batch) was prepared in a laboratory tilt mixer with a capacity of 100 litres. The mixture proportions of the

5 concrete are indicated in Table 6.

*Table 6: Mixture Proportions*

Water (kg/m <sup>3</sup> )	142.5
Cement (kg/m <sup>3</sup> )	475
Fine Aggregates (kg/m <sup>3</sup> )	790
Coarse Aggregates 14 mm (kg/m <sup>3</sup> )	1060
Water/Cement	0.30
Regular PNS	0.7% (6.8 l/m <sup>3</sup> )
Example 7	0.5-0.7% (4.7-6.6 l/m <sup>3</sup> )

The slumps of fresh concrete at 10, 30, 45, 60, 90 and 120 minutes with different cements at different dosages of superplasticiser were determined according to CSA-A23.2.5C Standards (ASTM C143). Figure 1 shows results obtained with Lafarge T-10 cement.

From Figure 1 it can be seen that beyond a certain threshold dosage, the superplasticiser of Example 7 conveys greatly improved slump retention compared to polynaphthalene sulfonate (REGULAR PNS).

Furthermore, in order to achieve better initial slump and longer slump retention on a 2-hour period, the required dosage of Example 7 is approximately 15% lower than with REGULAR PNS.

Slump losses measured with St. Lawrence cement and Holnam cement are shown in Figures 2 and 3, respectively.

With all tested cements, the superplasticiser of Example 7 maintains concrete workability during a 2-hour period. The dosage required is generally 15% lower than the dosage required for REGULAR PNS.

### ***Air entrainment***

Air content of concrete was determined at 10 and 90 minutes according to CSA-A23.2.4C Standards (ASTM C231). Concrete made with pNS as superplasticiser or with Example 7 showed less than 3% air  
5 content.

### ***Setting time***

Setting time was measured according to ASTM C-403 standard, on the mortar extracted from the fresh concrete by sieving. A comparison of  
10 setting times (initial and final) for concrete prepared with 0.7 wt% pNS versus concrete prepared with 0.6 wt% Example 7 is shown in Figure 4 (Lafarge T-10 cement).

### ***Tests on hardened concrete***

15 Compressive strength was determined according to CSA-A23.2.9C Standards (ASTM C39). Compressive strength measured at 1, 7 and 28 days for concrete prepared with 0.7 wt% pNS versus concrete prepared with 0.6 wt% Example 7 is shown in Figure 5. From Figure 5, it is evident that the superplasticiser of example 7 gives similar short and long term  
20 compressive strengths to those obtained with pNS.

### ***Comparison of a superplasticiser of the invention with an acrylic ester copolymer ("polycarboxylate") in fresh and hardened concrete***

#### ***25 Tests on fresh concrete***

The performance of a superplasticiser of the invention (Example 7) was compared with that of an acrylic ester copolymer, ("polycarboxylate"). The properties of fresh and hardened concrete were investigated under different cements at a water to cement ratio of 0.30.



The composition of the Lafarge T-10 cement tested is indicated Table 7. The fine aggregate was natural siliceous sand and the coarse aggregate was local metamorphic limestone having a maximum size of 20 mm.

**Table 7: Cement Composition**

	Lafarge Cement
SiO <sub>2</sub> (%)	20.6
Al <sub>2</sub> O <sub>3</sub>	4.4
Fe <sub>2</sub> O <sub>3</sub>	3.0
CaO	62.8
MgO	2.8
Na <sub>2</sub> O eq.	0.77
SO <sub>3</sub>	3.2
LOI	2.1

C <sub>3</sub> S	56
C <sub>2</sub> S	17
C <sub>3</sub> A	7
C <sub>4</sub> AF	9

Blaine Surface Area (m <sup>2</sup> /kg)	380
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Concrete (70ℓ or 170kg each batch) was prepared in a laboratory tilt mixer with a normal capacity of 100 litres. The mixture proportions of the  
5 concrete are indicated in Table 8.

**Table 8: Mixture Proportion**

Water	142.5
Cement (kg/m <sup>3</sup> )	475
Fine Aggregates (kg/m <sup>3</sup> )	790
Coarse Aggregates 14 mm (kg/m <sup>3</sup> )	1060
W/C	0.30
Polycarboxylate	0.2% (3.5 l/m <sup>3</sup> )
Example 7	0.6% (5.8 l/m <sup>3</sup> )

The slumps of fresh concrete at 10, 30, 45, 60, 90 and 120 minutes were determined according to CSA-A23.2.5C Standards (ASTM C143).

- 5 The results shown in Figure 6 were obtained with Lafarge T-10 cement. Figure 6 clearly shows that the superplasticiser of Example 7 gives a similar slump and slump life to the polycarboxylate superplasticiser.

#### ***Air entrainment***

- 10 Air content of concrete was measured at 10 and 90 minutes, according to CSA-A23.2.4C Standards (ASTM C231). The results are shown in Figure 7. It is clear that the superplasticiser of Example 7 does not cause significant air entrainment, whereas the polycarboxylate superplasticiser causes significant air entrainment. Air entrainment  
15 decreases the compressive strength of the resulting hardened concrete.

#### ***Setting time***

- The setting time of fresh concrete was determined according to ASTM C-403 Standard on the mortar extracted from the fresh concrete by  
20 sieving. The setting time for fresh concrete prepared with 0.6 wt%

Example 7 was compared with that obtained using 0.2 wt % polycarboxylate superplasticiser. The results are shown in Figure 8.

*Tests on hardened concrete*

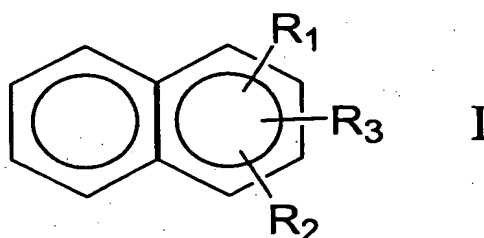
- 5           Compressive strength was measured according to CSA-A23.2.9C Standards (ASTM C39). Compressive strengths were measured at 1, 7 and 28 days for concrete prepared with 0.6 wt% superplasticiser of Example 7 and compared with those obtained for concrete prepared with 0.2% polycarboxylate superplasticiser. The results are shown in Figure 9.
- 10   It is clear that the superplasticiser of the invention gives similar short and long term compressive strengths to those obtained with polycarboxylate superplasticiser.

## WE CLAIM:

1. A polymer obtained by condensing with formaldehyde the monomers

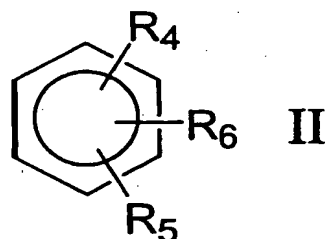
5 (A) a sulfonated aromatic compound; and

(B)



10 wherein  $R_1$ ,  $R_2$  and  $R_3$  may be substituted at any position of either aromatic ring, and are independently selected from H,  $(CH_2)_nOH$  ( $n=0$  to 6),  $N(CH_2CH_2OH)_2$ ,  $O(CH_2CH_2O)_nH$  ( $n=1$  to 113),  $CH_2O(CH_2CH_2O)_nCH_3$  ( $n=1$  to 113),  $O(CH_2CH_2O)_nCH_3$  ( $n=1$  to 113),  $(CH_2)_nCOOH$  ( $n=0$  to 6), and  $O(CH_2)_nCOOH$  ( $n=1$  to 6), and  $R_3$  is selected from H and  $CH_2OH$ ; and/or

15 (C)



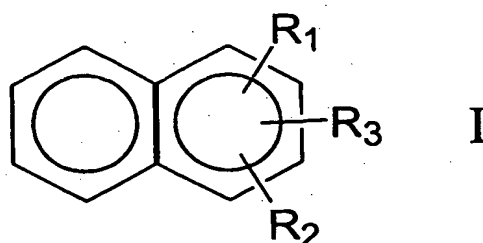
20 wherein  $R_4$ ,  $R_5$  and  $R_6$  may be substituted at any position of the benzene ring, and are independently selected from H,  $(CH_2)_nOH$  ( $n=0$  to 6),  $N(CH_2CH_2OH)_2$ ,  $O(CH_2CH_2O)_nH$  ( $n=1$  to 113),  $CH_2O(CH_2CH_2O)_nCH_3$  ( $n=1$  to 113),  $O(CH_2CH_2O)_nCH_3$  ( $n=1$  to 113),

$(\text{CH}_2)_n\text{COOH}$  ( $n=1$  to  $6$ ), and  $\text{O}(\text{CH}_2)_n\text{COOH}$  ( $n=1$  to  $6$ ), and  $\text{R}_6$  is selected from  $\text{H}$  and  $\text{NH}_2$ ;

wherein the polymer comprises at least one monomer that has at least one carboxyl group, and at least one monomer that has at least one hydroxyl group.

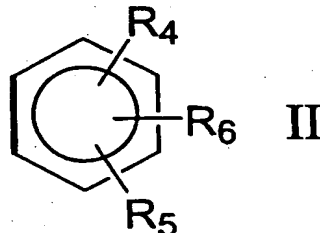
2. The polymer of claim 1, wherein monomer (A) is naphthalene sulfonate.
3. The polymer of claim 1 or 2, wherein  $\text{R}_1$  is  $\text{COOH}$ , at the 2-position, and  $\text{R}_2$  is  $\text{OH}$ , at the 3-position of the naphthalene nucleus.
4. The polymer of claim 3, wherein  $\text{R}_3$  is  $\text{CH}_2\text{OH}$ , at the 4-position of the naphthalene nucleus.
5. The polymer of any one of claims 1 to 4, comprising monomer (A) and monomer (B).
6. The polymer of any one of claims 1 to 4, comprising monomer (A) and monomer (C).
7. The polymer of any one of claims 1 to 4, comprising monomer (A), monomer (B) and monomer (C).
8. A superplasticiser for fresh concrete, the superplasticiser being obtained by condensing with formaldehyde the monomers (A) a sulfonated aromatic compound; and

(B)



wherein  $R_1$ ,  $R_2$  and  $R_3$  may be substituted at any position of either aromatic ring, and are independently selected from H,  $(CH_2)_nOH$  ( $n=0$  to 6),  $N(CH_2CH_2OH)_2$ ,  $O(CH_2CH_2O)_nH$  ( $n=1$  to 113),  $CH_2O(CH_2CH_2O)_nCH_3$  ( $n=1$  to 113),  $O(CH_2CH_2O)_nCH_3$  ( $n=1$  to 113),  $(CH_2)_nCOOH$  ( $n=0$  to 6), and  $O(CH_2)_nCOOH$  ( $n=1$  to 6), and  $R_3$  is selected from H and  $CH_2OH$ ; and/or

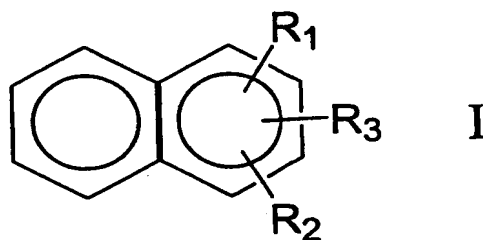
(C)



wherein  $R_4$ ,  $R_5$  and  $R_6$  may be substituted at any position of the benzene ring, and are independently selected from H,  $(CH_2)_nOH$  ( $n=0$  to 6),  $N(CH_2CH_2OH)_2$ ,  $O(CH_2CH_2O)_nH$  ( $n=1$  to 113),  $CH_2O(CH_2CH_2O)_nCH_3$  ( $n=1$  to 113),  $O(CH_2CH_2O)_nCH_3$  ( $n=1$  to 113),  $(CH_2)_nCOOH$  ( $n=1$  to 6), and  $O(CH_2)_nCOOH$  ( $n=1$  to 6), and  $R_6$  is selected from H and  $NH_2$ ;

wherein the superplasticiser comprises at least one monomer that has at least one carboxyl group, and at least one monomer that has at least one hydroxyl group.

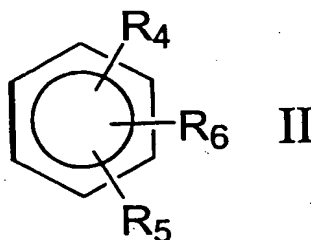
9. A method for decreasing the water requirement of a fresh concrete composition comprising adding to cement a plasticising amount of a superplasticiser according to claim 8.
- 5 10. A dry cement composition, comprising cement and a superplasticiser according to claim 8.
11. A wet fresh concrete composition comprising a dry cement composition according to claim 10 mixed with water.
- 10 12. A cured concrete product produced by curing a wet fresh concrete composition according to claim 11.
13. A superplasticiser for fresh concrete, the superplasticiser being  
15 obtained by condensing a homopolymer of a sulfonated aromatic compound with formaldehyde and (B)



- 20 wherein  $R_1$ ,  $R_2$  and  $R_3$  may be substituted at any position of either aromatic ring, and are independently selected from H,  $(CH_2)_nOH$  ( $n=0$  to 6),  $N(CH_2CH_2OH)_2$ ,  $O(CH_2CH_2O)_nH$  ( $n=1$  to 113),  $CH_2O(CH_2CH_2O)_nCH_3$  ( $n=1$  to 113),  $O(CH_2CH_2O)_nCH_3$  ( $n=1$  to 113),  $(CH_2)_nCOOH$  ( $n=0$  to 6), and  $O(CH_2)_nCOOH$  ( $n=1$  to 6), and  $R_3$  is  
25 selected from H and  $CH_2OH$ ; and/or



(C)



wherein  $R_4$ ,  $R_5$  and  $R_6$  may be substituted at any position of the benzene ring, and are independently selected from H,  $(CH_2)_nOH$  ( $n=0$  to 6),  $N(CH_2CH_2OH)_2$ ,  $O(CH_2CH_2O)_nH$  ( $n=1$  to 113),  $CH_2O(CH_2CH_2O)_nCH_3$  ( $n=1$  to 113),  $O(CH_2CH_2O)_nCH_3$  ( $n=1$  to 113),  $(CH_2)_nCOOH$  ( $n=1$  to 6), and  $O(CH_2)_nCOOH$  ( $n=1$  to 6), and  $R_6$  is selected from H and  $NH_2$ ;

wherein the superplasticiser comprises at least one monomer that has at least one carboxyl group, and at least one monomer that has at least one hydroxyl group.

14. A superplasticiser according to claim 8, obtained by condensing with formaldehyde monomer (A) and monomer (B), wherein monomer (A) is naphthalene sulfonate, and monomer (B) is 3-hydroxy-2-naphthoic acid.
15. A superplasticiser according to claim 14, wherein monomer (A) is used at about 94 molar % and monomer (B) is used at about 6 molar %, based on the total number of moles of monomer (A) and monomer (B).
16. A superplasticiser according to claim 14, wherein monomer (A) is used at about 91 molar % and monomer (B) is used at about 9

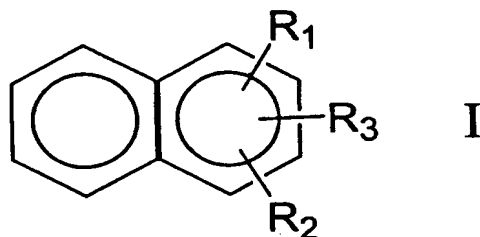
molar %, based on the total number of moles of monomer (A) and monomer (B).

17. A process for preparing a superplasticiser of claim 8, the process comprising:

condensing with formaldehyde the monomers

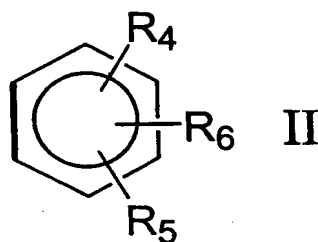
(A) a sulfonated aromatic compound; and

(B)



wherein R<sub>1</sub>, R<sub>2</sub> and R<sub>3</sub> may be substituted at any position of either aromatic ring, and are independently selected from H, (CH<sub>2</sub>)<sub>n</sub>OH (n=0 to 6), N(CH<sub>2</sub>CH<sub>2</sub>OH)<sub>2</sub>, O(CH<sub>2</sub>CH<sub>2</sub>O)<sub>n</sub>H (n=1 to 113), CH<sub>2</sub>O(CH<sub>2</sub>CH<sub>2</sub>O)<sub>n</sub>CH<sub>3</sub> (n=1 to 113), O(CH<sub>2</sub>CH<sub>2</sub>O)<sub>n</sub>CH<sub>3</sub> (n=1 to 113), (CH<sub>2</sub>)<sub>n</sub>COOH (n=0 to 6), and O(CH<sub>2</sub>)<sub>n</sub>COOH (n=1 to 6), and R<sub>3</sub> is selected from H and CH<sub>2</sub>OH; and/or

(C)



wherein R<sub>4</sub>, R<sub>5</sub> and R<sub>6</sub> may be substituted at any position of the benzene ring, and are independently selected from H, (CH<sub>2</sub>)<sub>n</sub>OH (n=0 to 6), N(CH<sub>2</sub>CH<sub>2</sub>OH)<sub>2</sub>, O(CH<sub>2</sub>CH<sub>2</sub>O)<sub>n</sub>H (n=1 to

113),  $\text{CH}_2\text{O}(\text{CH}_2\text{CH}_2\text{O})_n\text{CH}_3$  ( $n=1$  to 113),  $\text{O}(\text{CH}_2\text{CH}_2\text{O})_n\text{CH}_3$  ( $n=1$  to 113),  $(\text{CH}_2)_n\text{COOH}$  ( $n=1$  to 6), and  $\text{O}(\text{CH}_2)_n\text{COOH}$  ( $n=1$  to 6), and  $\text{R}_6$  is selected from H and  $\text{NH}_2$ ;

5            wherein at least one monomer has at least one carboxyl group, and at least one monomer has at least one hydroxyl group.

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Figure 1

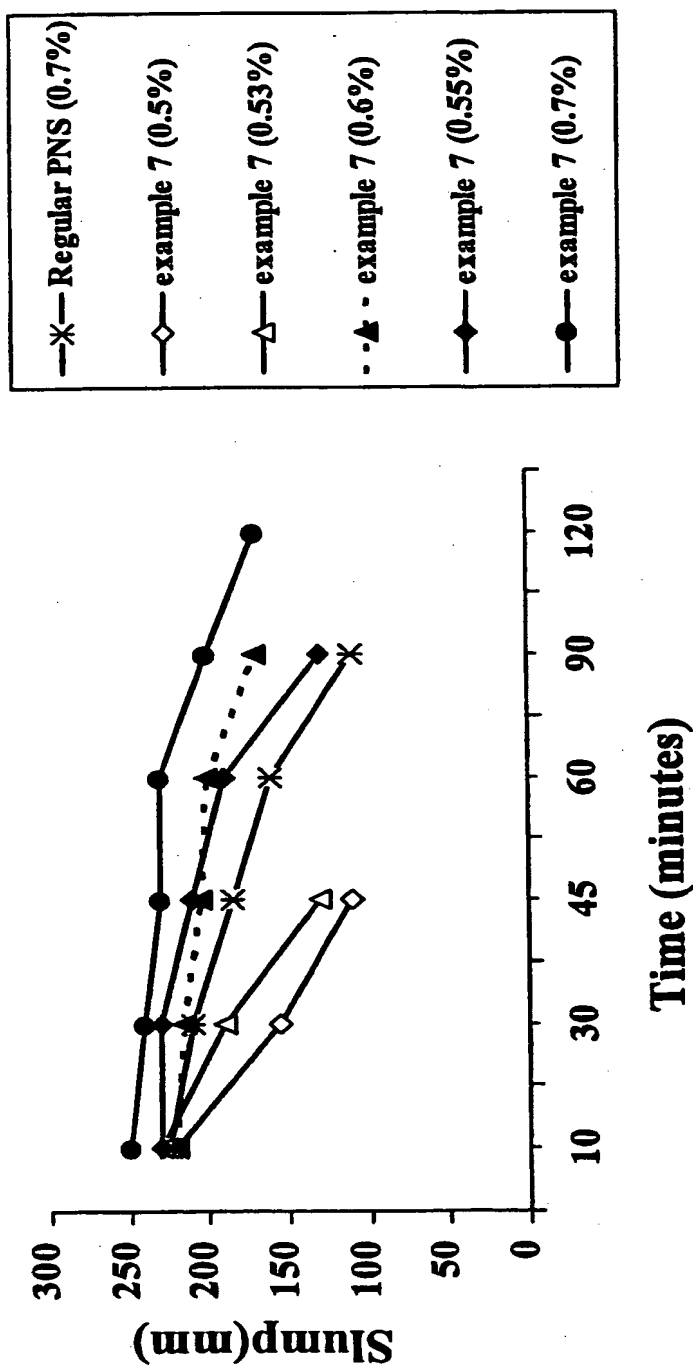
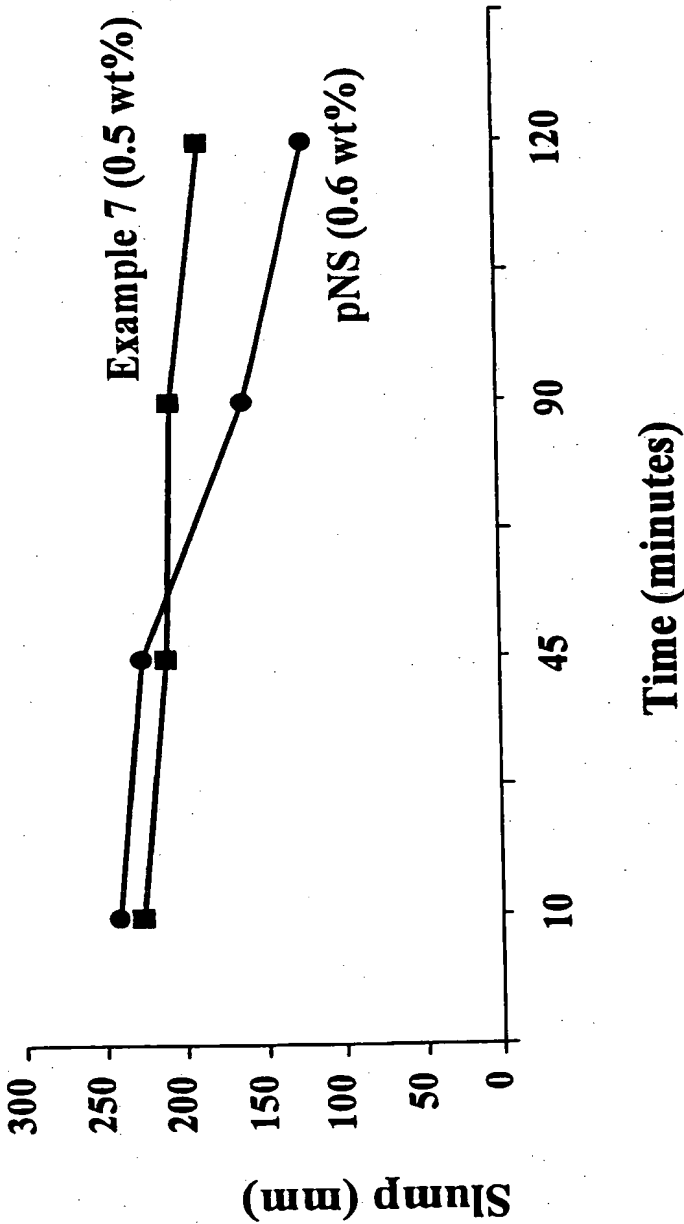


Figure 2



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Figure 3

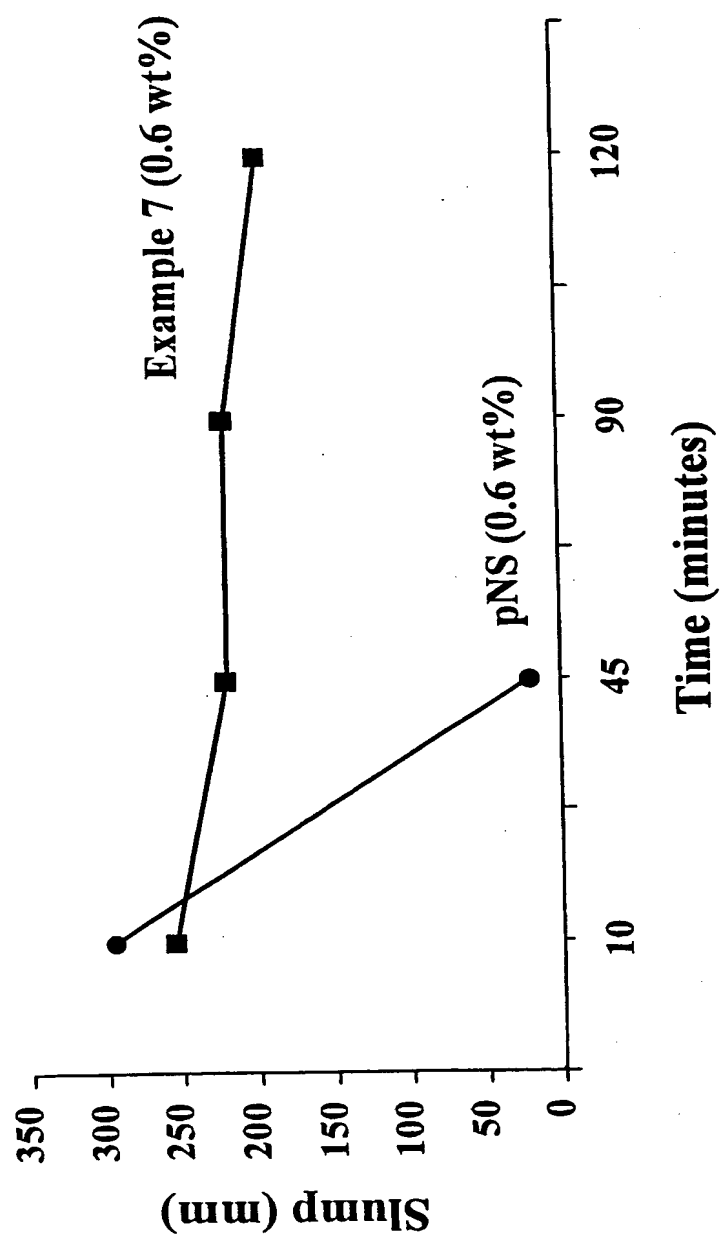
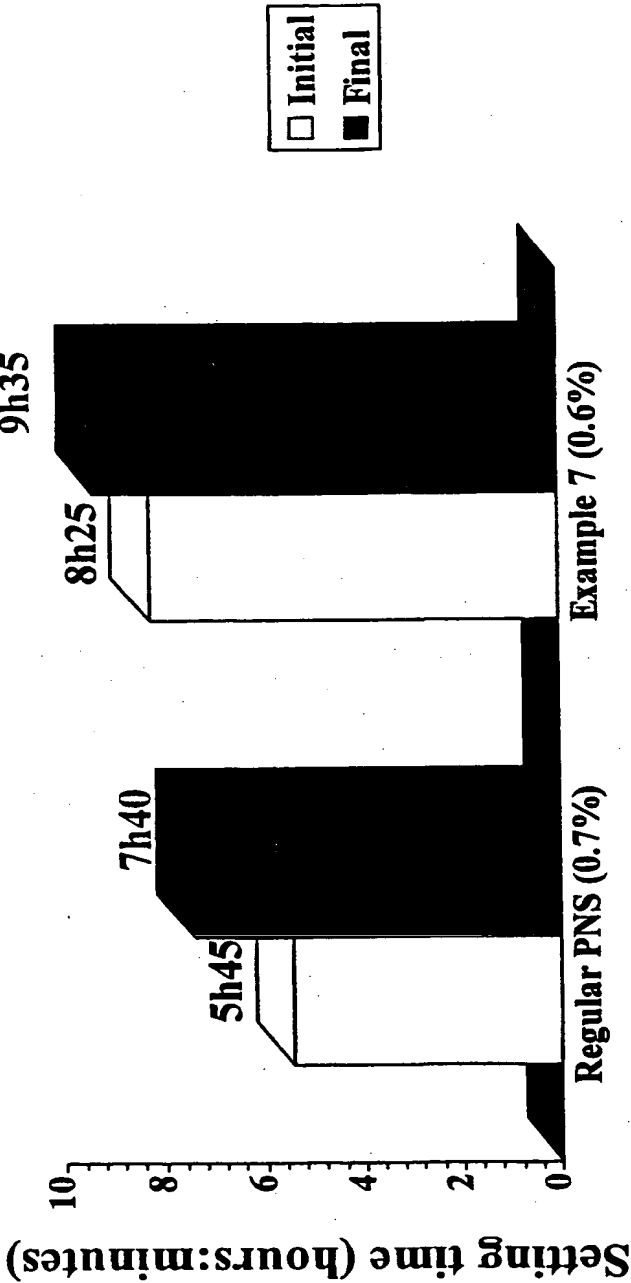
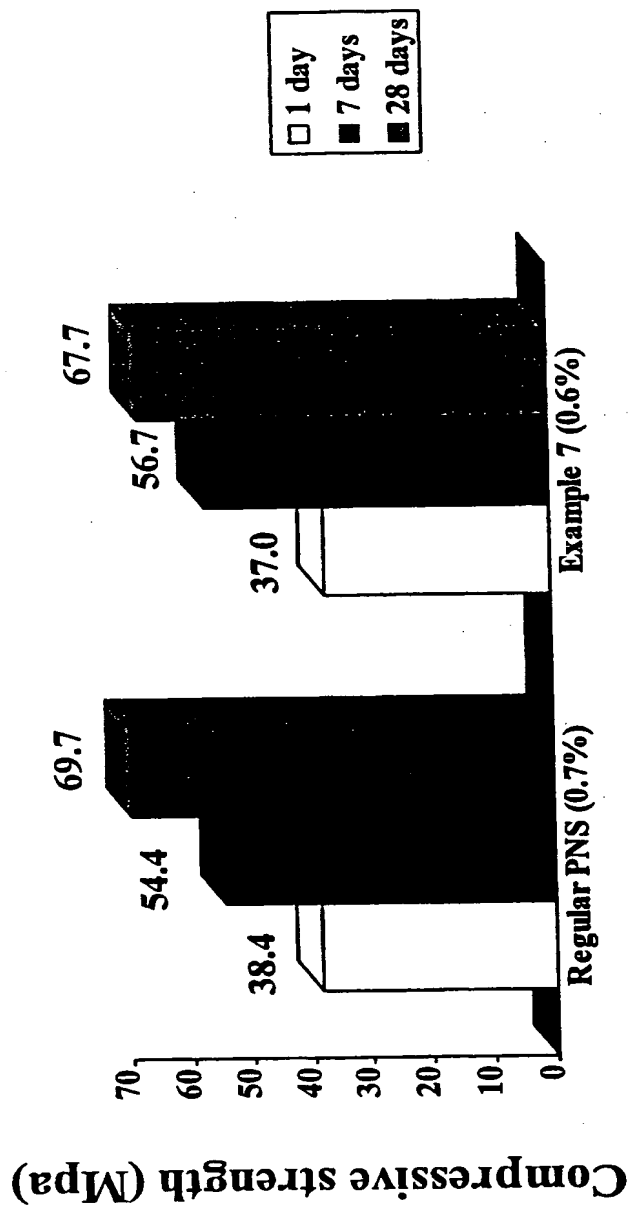


Figure 4



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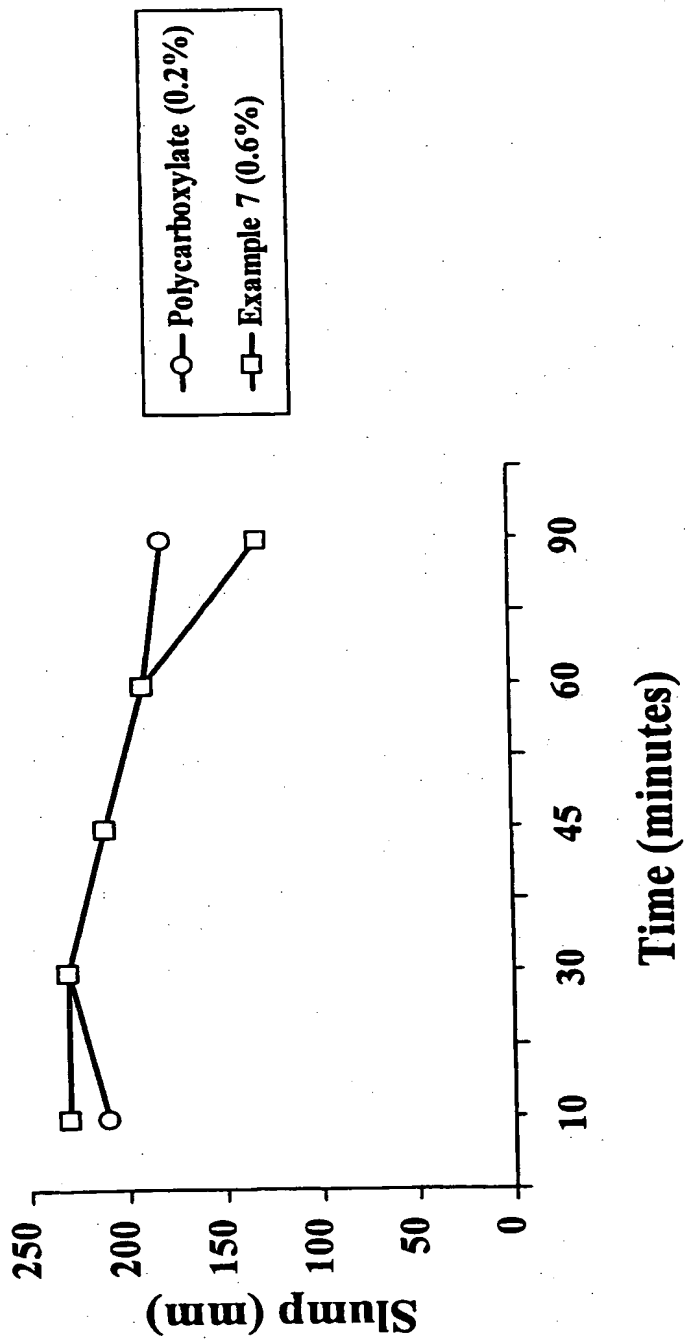
Figure 5





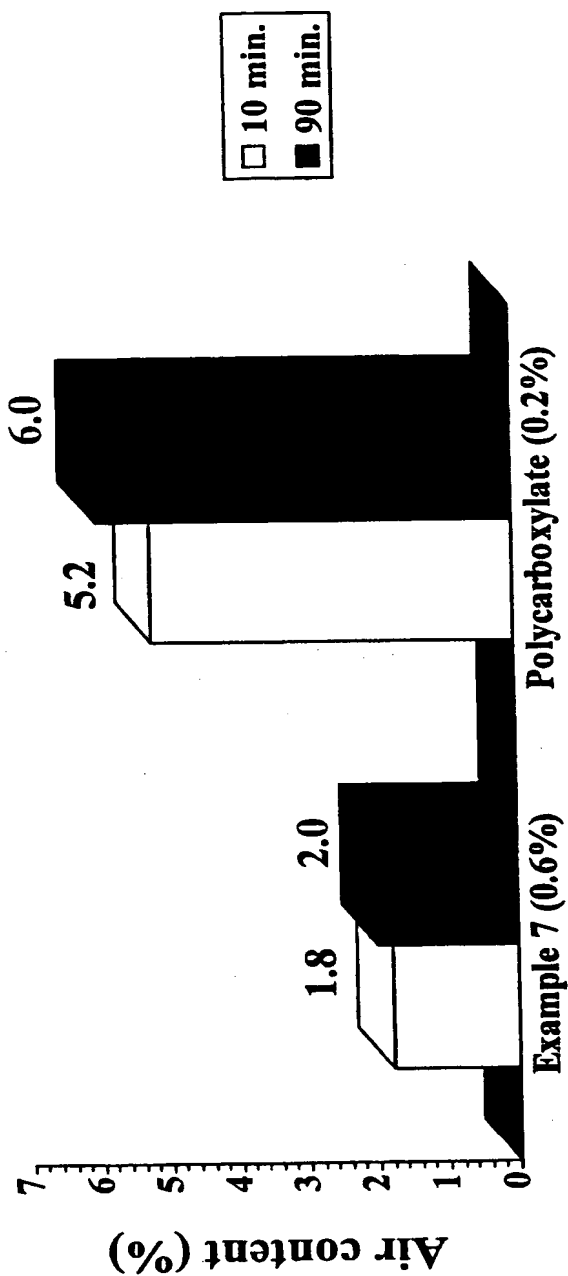
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Figure 6



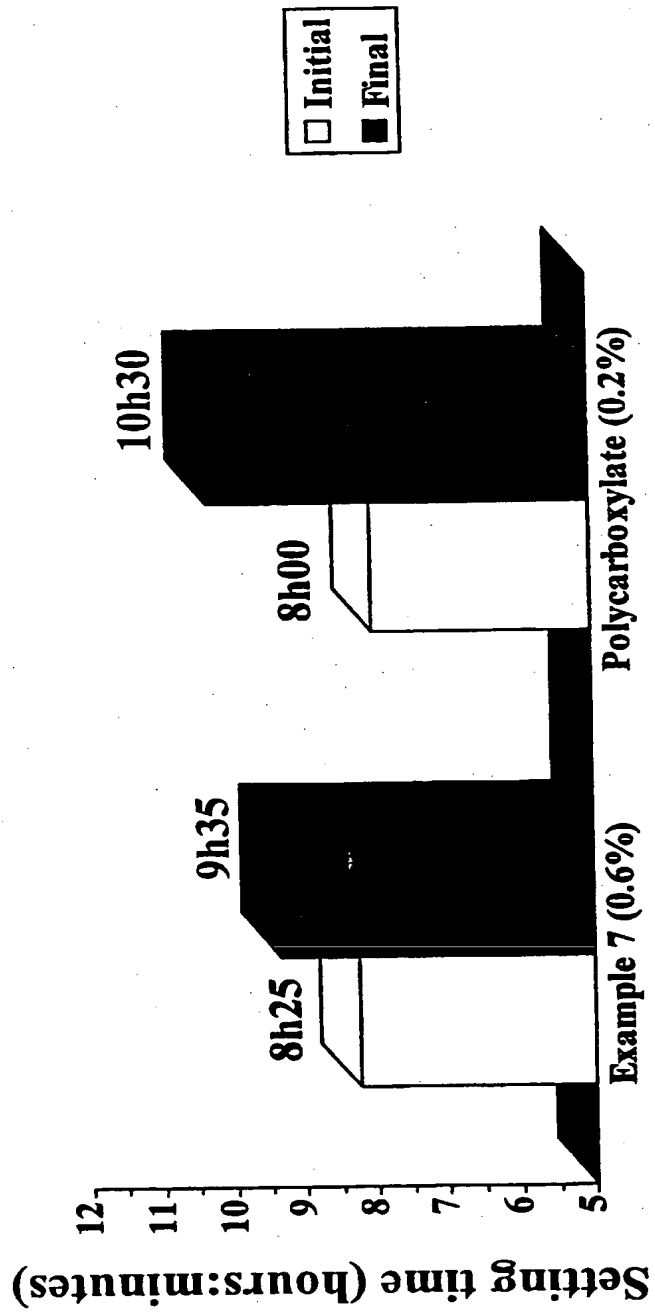
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Figure 7



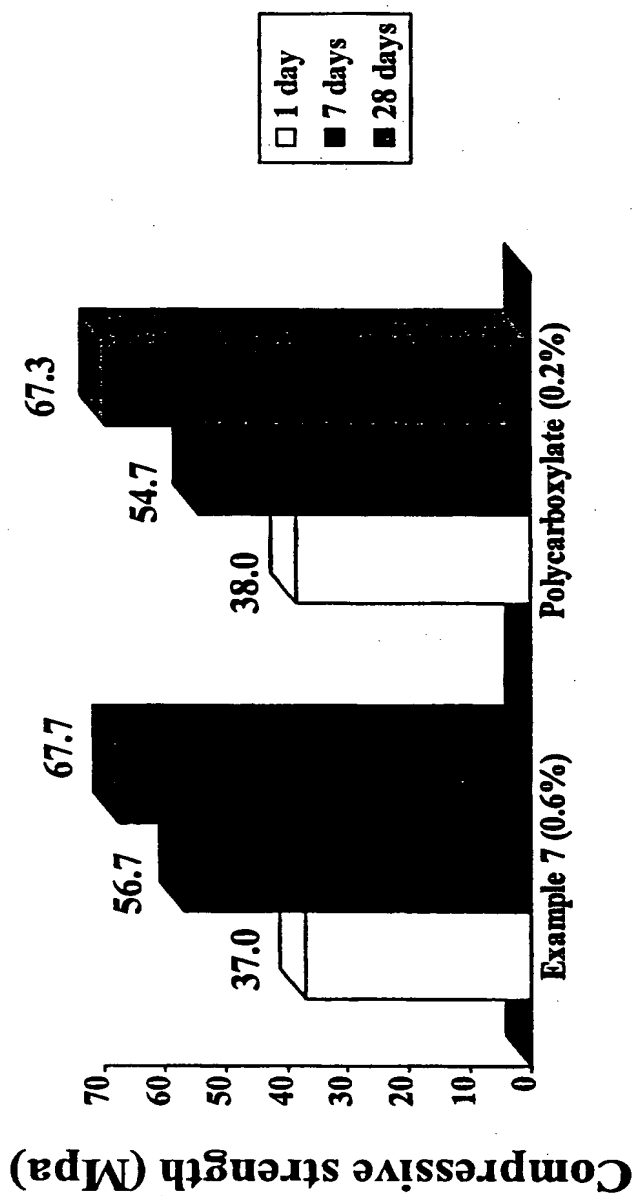
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Figure 8



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Figure 9



# INTERNATIONAL SEARCH REPORT

In. ational Application No

PCT/CA 00/00639

**A. CLASSIFICATION OF SUBJECT MATTER**  
IPC 7 C08G8/18 C04B24/22

According to International Patent Classification (IPC) or to both national classification and IPC

**B. FIELDS SEARCHED**

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 C08G C04B C94B

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data, PAJ, CHEM ABS Data

**C. DOCUMENTS CONSIDERED TO BE RELEVANT**

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP 0 780 348 A (KAO CORP) 25 June 1997 (1997-06-25) cited in the application page 9; example 9 ---	1,2, 7-13,17
X	DATABASE WPI Section Ch, Week 198740 Derwent Publications Ltd., London, GB; Class A93, AN 1987-283628 XP002147200 & SU 1 296 536 A (KAZAN ENG-CONS INST), 15 March 1987 (1987-03-15) abstract ---	1,6, 8-13,17
X	US 1 989 802 A (HESTER W.F ET AL) 5 February 1935 (1935-02-05) claim 6; example 1 --- -/--	1,2,6

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

\* Special categories of cited documents :

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Date of the actual completion of the international search

12 September 2000

Date of mailing of the international search report

28/09/2000

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# INTERNATIONAL SEARCH REPORT

In. .ational Application No

PCT/CA 00/00639

## C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	GB 430 343 A (JAMES YATE JOHNSON) example 1 column 2, line 70 - line 75 ---	1,2,6
X	DE 22 64 395 A (SANDOZ AG) 28 June 1973 (1973-06-28) claims 1,7 ---	1,2,6
A	US 4 391 645 A (MARCELLIS ALPHONSO W ET AL) 5 July 1983 (1983-07-05) claim 1 ---	1-17
A	CHEMICAL ABSTRACTS, vol. 103, no. 16, 1985 Columbus, Ohio, US; abstract no. 128073p, BATRAKOV V.G ET AL: "Superplasticizer-liquefier SMF " page 291; XP002147199 abstract & BETON ZHELEZOBETON, vol. 5, 1985, pages 20-21, Moscow -----	1-17

# INTERNATIONAL SEARCH REPORT

In :ational Application No

PCT/CA 00/00639

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
EP 0780348	A	25-06-1997	NONE	
SU 1296536	A	15-03-1987	NONE	
US 1989802	A	05-02-1935	NONE	
GB 430343	A		NONE	
DE 2264395	A	28-06-1973	NONE	
US 4391645	A	05-07-1983	NONE	

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